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ACRYLONITRILE POLYMER SOLUTIONS AND PROCESS OF SHAPING THE SAME

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This invention relates to solutions of polyacrylonitrile and more particularly to solutions which are of particular utility in the preparation of filamentary material.

The solubility of acrylonitrile polymers containing major amounts, i. e., 85% or more, of acrylonitrile in strong aqueous salt solutions such as solutions of thiocyanates is well known. See for example U. S. Patents 2,140,921, 2,404,714, 2,404,716, British Patent 636,476. Such solutions are of advantage in that they may be readily prepared from finely divided acrylonitrile polymer of average molecular weight, the solvent salts are generally cheap and available, and as has been shown in U. S. 2,404,714 and 2,404,716, fibers or films may be formed by extrusion of the solution into an aqueous coagulating bath. However, the products obtained are spongy, weak, undrawable and unsatisfactory for conventional film or filament applications. Furthermore, these highly concentrated solutions have certain further disadvantages in the fabrication of filamentary material. Thus, as shown in British Patent 636,476, the concentration of salt, such as zinc chloride, should be at least 60% and preferably 70–75%. Such a solution contains a very high concentration of salt and the concentration of polymer is generally low. Increasing the polymer concentration results in a viscous solution which is difficult to employ in spinning. Solutions in which the polymer concentration is low give coagulated fibers or films which are deficient in strength.

This invention has as an object the preparation of aqueous solutions of acrylonitrile polymers of viscosity suitable for spinning. A further object is the preparation of useful fibers and films from such solutions. Other objects will appear hereinafter.

These objects are accomplished by the invention of aqueous salt solutions containing from 8 to 25%, by weight thereof, of acrylonitrile polymers containing 32 to 50% of the salt, preferably an alkali metal thiocyanate or an alkaline earth metal thiocyanate, acrylonitrile polymer in amount from 25 to 100% of the weight of the salt, at least 5%, preferably at least 10%, but not more than 35% water, 15 to 35% of a neutral organic oxy compound containing not more than six carbons, liquid at room temperature, miscible with water in all proportions at room temperature, having a carbon to oxy oxygen ratio of from 1:1 to 3:1, and containing only carbon, hydrogen, and oxygen, said solution having a ratio of salt to acryonitrile polymer of from 1:1 to 4:1, which solutions have superior properties for the preparation of coagulated structures.

The solutions of this invention are readily obtained by mixing the salt, water, alcohol or ether and polymer. By the use of the selected oxygenated compounds, it is generally unnecessary that elevated temperatures be employed to effect solution of the compositions.

The following examples in which parts are by weight are illustrative of the invention.

Example I

A solution of 52.3 parts of sodium thiocyanate, 37.6 parts of calcium thiocyanate, 75.1 parts of water and 45 parts of dioxane is cooled to 0° C. and poured over 30 parts of a powdered copolymer of acrylonitrile and 2-methyl-5-vinylpyridine in the proportions of 95/5. The system is rapidly stirred immediately to get good wetting of the polymer before the system becomes viscous. On warming to room temperature a clear solution is obtained. This solution containing 12.5% polymer, 21.9% sodium thiocyanate, 15.6% calcium thiocyanate, 31.2% water and 18.8% dioxane is filtered, deaerated, and poured into the spinning bomb.

This solution at 25° C. is spun at a pump speed of 5.2 cc./min. through a 40-hole; 10 mil hole size, spinneret into water at 25–30° C. The filaments coagulate quickly and no trouble with stuck filaments is encountered. After a bath travel of 20 inches, the filaments are collected on a bobbin at a windup speed of 14 ft./min. Under these conditions there is almost no tension on the filaments (only enough to keep them taut in the coagulating bath) indicating that little, if any, stretching or orientation occurs in the coagulating bath. Water is dripped on the package of gel yarn during the windup operation to prevent the gel yarn from drying out. The yarn is soaked overnight in water and then dried in a relaxed state. The dried yarn is drawn to a ratio of 10/1 in water at 100° C. The yarn, in skein form, is then exposed to water at 100° C. for an hour (boil-off treatment). This boiled-off yarn has a tenacity of 1.8 g./d. at 17% elongation.

Example II

A solution of a copolymer of acrylonitrile and 2-vinylpyridine in the proportions of 95/5 is prepared by the same technique as described for the solution of Example I. Methanol is used in place of dioxane in this solution, and the final clear solution consists of 12.5% polymer, 21.8% sodium thiocyanate, 15.7% calcium thiocyanate, 31.2% water and 18.8% methanol.

The solution at 25° C. is spun at a pump speed of 2 cc./min. through a 30-hole (7 mil hole size) spinneret into a water coagulating bath at 25° C. A short bath travel of only three inches is used. The yarn passes under a free-rolling roller, located close to the spinneret, and out of the bath in a direction at right angles to the original direction of travel. The yarn is then passed around a glass rod, to give a snubbing action, and continues in a line parallel to the original direction of travel to a windup bobbin. Water is dripped on the windup bobbin to prevent the gel yarn from drying out during the windup operation. The gel yarn is exposed to water at 25° C. overnight to assure complete removal of salt. One package of yarn is collected under only slight tension at a windup speed of 3 ft./min. and another package is collected at a windup speed of 9 ft./min. This latter yarn is under considerable tension between the snubbing rod and the windup. These yarns are given a 2 Z (two turns per inch) twist while in the gel state and then are dried at 25° C. on a bobbin. It is particularly important to carry out the twisting operation on the gel yarn rather than the dried yarn if the yarn has been subjected to little or no stretching in the coagulating bath, as in the case of the former yarn. This type of yarn is somewhat brittle on drying out and accordingly some trouble is encountered with broken filaments if the twisting operation is carried out on the dried yarn; whereas, the gel yarn is not brittle and can be satisfactorily twisted. Yarn which has been stretched in the coagulating bath, as in the case of the latter yarn, is much tougher on drying out and may be twisted in the dried condition without any trouble.

The yarn collected at a windup speed of 3 ft./min. and dried on a bobbin is drawn to a ratio of 7.5/1 in